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Acknowledgments

We gratefully acknowledge the NASA Glenn Research Center for financial support cooperative agreement NCC3-947.

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Abstract

The development of thin-film solar cells on flexible, lightweight, space-qualified substrates provides an attractive cost solution to fabricating solar arrays with high specific power (W/kg). Thin-film fabrication studies demonstrate that ternary single source precursors (SSP's) can be used in either a hot or cold-wall spray chemical vapour deposition (CVD) reactor, for depositing CuInS₂, CuGaS₂ and CuGaInS₂ at reduced temperatures (400 to 450 °C), which display good electrical and optical properties suitable for photovoltaic (PV) devices. X-ray diffraction studies, energy dispersive spectroscopy (EDS)

and scanning electron microscopy (SEM) confirmed the formation of the single phase CIS, CGS, CIGS thin-films on various substrates at reduced temperatures.

1. Introduction

Photovoltaic modules based on I-III-VI₂ ternary chalcopyrite absorber layers, have been the focus of intense investigation for over two decades. The use of chalcopyrite absorbers are highly appealing since their bandgaps correlate well to the maximum photon power density in the solar spectrum for both terrestrial (AM 1.5), and space applications (AM0), while displaying long term stability and excellent radiation tolerance [1–4]. Additionally, by adjusting the percent atomic composition of either Ga for In and/or S for Se, the bandgap can be tuned from 1.0 to 2.4 eV, thus permitting the fabrication of multi-junction solar cells [5]. One of the key technical issues outlined in the 2001 US Photovoltaic roadmap is the need to develop low cost, high throughput manufacturing for high-efficiency thin film solar cells. Thus, an important step for device fabrication for high specific power (WKg⁻¹) thin film solar cells, is deposition onto flexible lightweight substrates. A novel approach is the use of ternary I-III-VI₂ single source precursors (SSP's) in a spray chemical vapour deposition (CVD) process. Although, a rich and diverse array of binary SSP's [6–8] are reviewed and tested, the number of known ternary SSP's is still limited, as is their use in deposition processes [7]. Hence, in this paper we highlight recent advances, summarizing a highly promising technique for thin film growth, via molecular design of ternary SSP's for use in various spray CVD processes.

2. Experimental

The SSP's are synthesized based on a modification of the procedure reported by Kanatzidis [9,10]. Films were deposited on conventional soda-lime, corning 7059 slides, Si(100), and Si(111) substrates. Thin films of CuGaS₂ and CuGa_xIn_yS₂ were deposited using [$\{PPh_3\}_2Cu(SET)_2In(SET)_2$] **1** and the new Ga analogue **2**, which was not fully characterized [11] in a custom-made horizontal hot-wall spray CVD reactor [9,12,14], whereas films of CuInS₂ were deposited using [$\{PPh_3\}_2Cu(SET)_2In(SET)_2$] **3** in a custom-made vertical cold wall spray CVD reactor [13]. The CuGaS₂ deposition was conducted using a 0.011 M mixed toluene/methylene bromide solution (86 vol % toluene) (1.3 mmol; 1.10 g); substrate temperature of 450±5 °C with an Ar carrier-gas flow rate of 4.0 L/min [11]. The Cu(In,Ga)S₂ deposition was conducted with similar deposition parameter used for CuGaS₂ above except, a 0.01 M toluene solution of the In **1** and Ga **2** SSP's in an attempt to achieve a ratio of In_{0.75}Ga_{0.25}. Films were characterized by optical transmission spectroscopy (Perkin Elmer, Lambda-19, Cary 5 UV-VIS-NIR spectrophotometer), scanning electron microscopy-EDS (Hitachi S-3000N), X-ray diffraction (Philips PW3710 : Cu K α , 1.541 Å) and Van der Pauw four point probe system (Bio-Rad HL5500PC). Reported SEM-EDS measurements are accurate to ±3%.

3. Results and Discussion

We have previously reported the preparation and utility of ternary SSP's to the semiconductor CuInS₂ in a horizontal hot wall spray CVD process [9,12,14]. We now report, the preparation of ternary SSP for the fabrication of thin-film CuGaS₂, in addition, the versatility of ternary SSP's in a spray CVD process is demonstrated by their use in either a hot and cold wall reactors of either horizontal or vertical configuration (Fig.1). Spray CVD studies utilizing the new Ga SSP in a toluene/CH₂Br₂ solution

afforded well-adhered, visually smooth and optically transparent dense thin film exhibiting a pink-green surface tint. X-ray diffraction (XRD) analysis confirmed the film to be 112 oriented, tetragonal single phase CuGaS₂ (Fig. 2). The 220/204 reflections and the 312/116 reflections were split consistent with the tetragonal distortion of the crystal lattice [15]. Lattice parameters *a* and *c* were calculated from X-ray *d* spacings, ($1/d^2 = 1/a^2 (h^2 + k^2) + l^2/c^2$; where *h*, *k*, and *l* are the Miller indices of individual reflections [16]), Table 1. Comparison of the data collected from the CuGaS₂ thin film shows they are in good agreement with the JCPDS reference values for single-crystal CuGaS₂ and with those reported in literature [17].

SEM images reveal the films are dense with an average grain size of 410 nm, with a columnar grain structure (Fig. 3(c) to (d)). The surface microstructure consisted of faceted grains many of which exhibited a trigonal shape (Fig. 3(a) to (b)), which occurs as a result of close-packed intersecting (112) faces of the chalcopyrite lattice. These are the lowest surface-energy faces and typically control chalcopyrite morphology [8,18,19].

The resistivity for the CuGaS₂ thin film samples deposited at 450 °C on fused silica were determined using the four-point probe method [20] and found to be 15.6(4) Ω·cm, which is comparable to those reported in literature [20,21]. The optical bandgap of the films were determined from the derivative of the optical transmittance data (Fig. 4), which correlates well with the reported direct band gap of CuGaS₂, *E_g* = 2.43 eV [22].

Initial studies using a homogeneous toluene solution of the two ternary SSP's **1** (0.0075 M) and **2** (0.0025 M) for fabrication of an alloy film Cu(In:Ga)S₂ was also investigated [11]. Although a thin-film was deposited, composition and microstructure varied along the length of the thin film. XRD reflections representing the 112 planes were broad and complicated by the presence of an unidentified reflection in that region. The 220/204 planes was represented by a single unresolved reflection that yielded an average grain size of ~40 nm. The relative contribution of Ga and In to the multinary structure was determined by comparing the 2-theta values for this reflection in the multinary pattern to those in the patterns of the ternary end-members, CuInS₂ and CuGaS₂ (Fig. 5(f)). The composition of each metal was assumed to vary linearly with 2-theta from 100% In to 100% Ga based on Vegard's Law. The tetragonal splitting was neglected in the CuGaS₂ pattern by averaging the 2-theta values for the 220 and the 204 reflections. The atomic percent of Ga in the film was found to increase along the length of the film (front to rear), (Fig. 5). A uniform composition over large areas was not achieved and none of the compositions were close to the expected In_{0.75}Ga_{0.25} ratio. The variation in film composition is understandable since the Ga derivative decomposed at higher temperatures than its In analogue. Therefore, using two SSP's with matching thermal profiles can provide an effective means for depositing multi-ternary films.

The flexibility of the SSP's in a spray CVD has been further demonstrated by their use in a cold wall vertical CVD reactor [13]. The XRD data obtained from the film grown using [**3**] in a cold-wall reactor revealed the typical tetragonal chalcopyrite CuInS₂ phase with a 112 preferred orientation. The band-gap for the film grown from the liquid precursor, derived from a plot of (α *E*)² versus *E* (Fig. 6), was found to be ~1.46 eV. Although annealing the film showed a shift to a higher gradient band edge, it was found to have minimal effect on the observed

bandgap. SEM-EDS analysis showed the CuInS₂ thin-film to be near stoichiometric with atomic percents for Cu, In, and S as 26, 24, and 50 ($\pm 3\%$), respectively.

4. Summary

The versatility of the ternary SSP's is clearly demonstrated by the preparation of various multi-ternary semiconductors. Spray CVD using SSP's is a mild, simple, clean, and scalable technique for depositing CuME₂ (E= VI, M= III) thin-films at reduced temperatures. Although tests for the deposition of the wide bandgap alloy Cu(Ga:In)S₂, led to a non-homogenous film composition, it is evident the use of two SSP's with similar thermal profiles, consistent film stoichiometry can be achieved. Spray CVD in conjunction with SSP design provides a proof-of-concept for a high manufacturability process. The work reported here on the molecular design of SSP's for their use in a spray CVD process although still in its infancy, undoubtedly shows it as a mass producible, cost effective method for fabricating commercial thin film PV devices.

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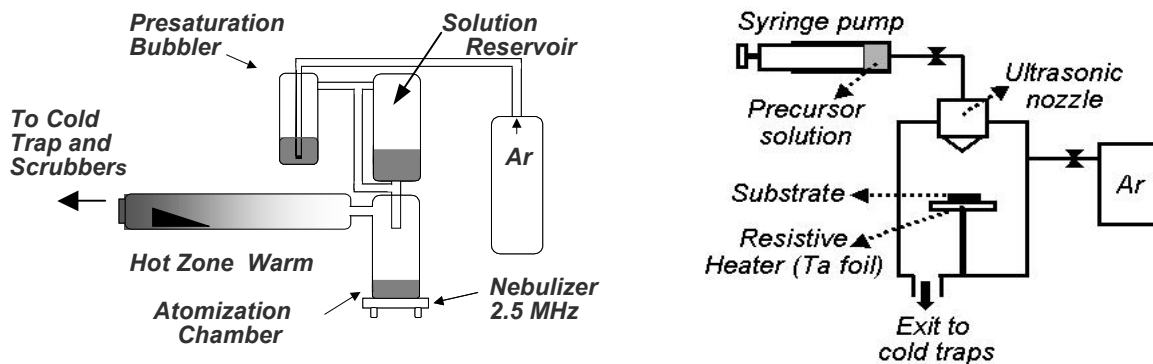


Fig. 1 Schematic of horizontal hot wall and vertical cold wall spray CVD reactors.

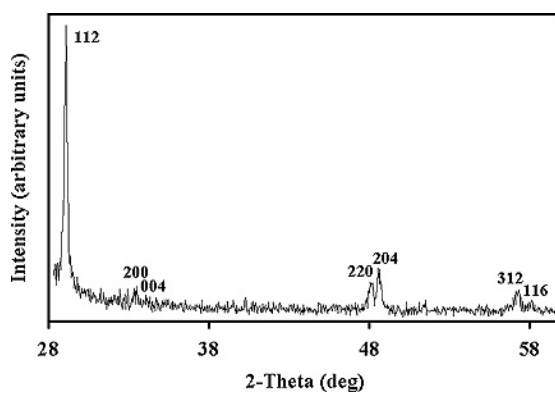


Fig. 2 XRD pattern XRD of spray-CVD grown CuGaS₂ film on Si(111). Reflections correspond to those reported for Gallite in JCPDS reference # 25-0279

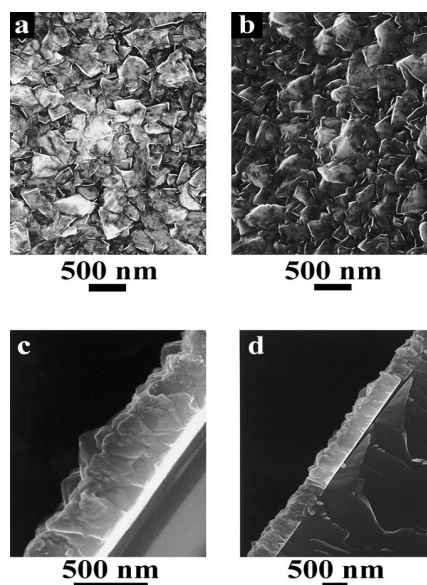


Fig. 3 SEM of CuGaS_2 films deposited by spray CVD. a) surface view. b) Surface view; 30° tilt showing triangular shape characteristic of 112-oriented crystals. c) and d) edge views showing roughly columnar crystal-growth pattern.

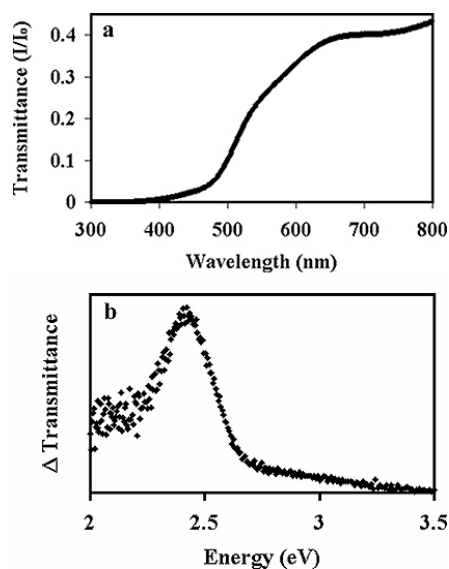


Fig. 4 a) Transmittance vs. wavelength for CuGaS_2 thin film; (I = transmitted, I_0 = incident power; b) Plot of the derivative of the transmission data vs. energy.

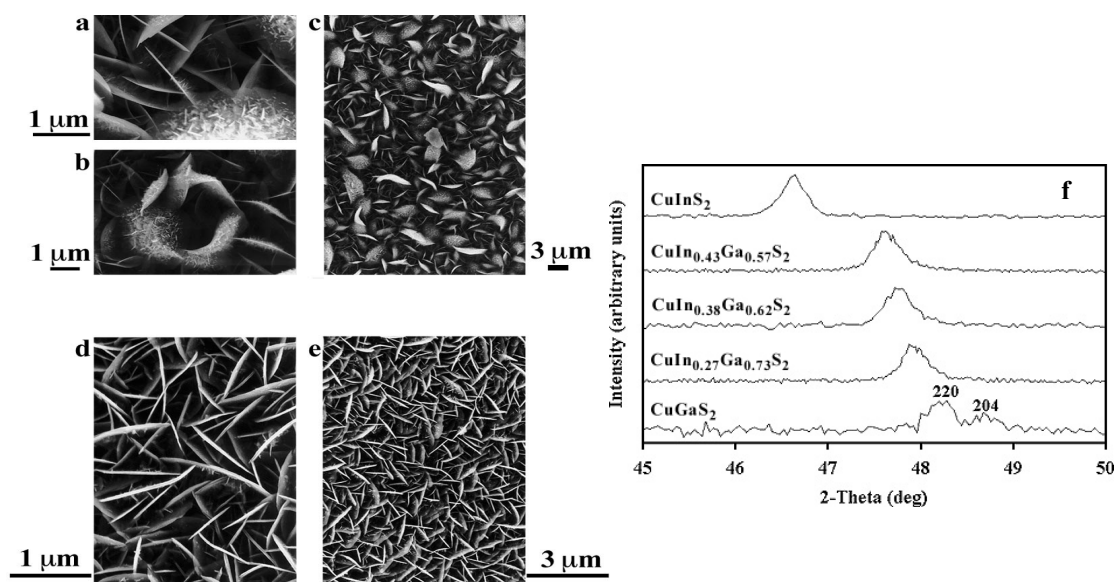


Fig. 5 SEM images of the alloy film showing the variation in microstructure with composition. a–c) Film deposited in the first centimeter: $\text{CuIn}_{0.43}\text{Ga}_{0.57}\text{S}_2$. d and e) Film deposited in the last centimeter: $\text{CuIn}_{0.27}\text{Ga}_{0.73}\text{S}_2$. f) XRD spectra highlighting the 220/204 reflections of a CuGaS_2 film (bottom; $T_s = 450\text{ }^\circ\text{C}$), a CuInS_2 film (top; $T_s = 400\text{ }^\circ\text{C}$) and alloy films having In_xGa_y contents in the range: $\text{In}_{0.43}\text{Ga}_{0.57} - \text{In}_{0.27}\text{Ga}_{0.73}$ (on fused silica).

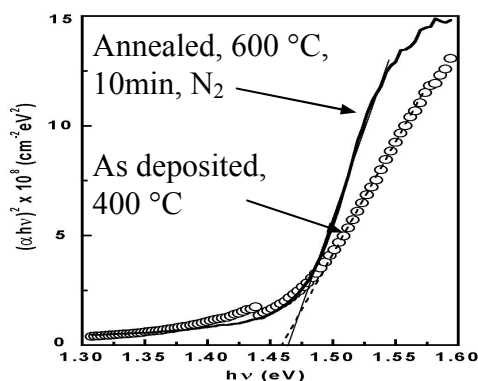


Fig. 6 A plot of $(\alpha E)^2$ vs. E for the film grown in the cold-wall reactor, (α is an absorption coefficient estimated from the optical transmittance data and E is a photon energy).

Table 1. Comparison of thin-film and single-crystal CuGaS₂ lattice parameters, a and c , c/a , and the distortion parameter x . The d spacing of the 220 reflection was used to calculate a , and the d spacing of the 112 reflection was used with the calculated lattice parameter a to determine c . ($x = 2 - c/a$, given that a hypothetical c/a ratio of 2 would result in the *absence* of any tetragonal distortion)

| a (Å) | c (Å) | a/c | x | Thin film fabrication method |
|---------------------------|---------------------------|-------------------------|-----------------------|---|
| 5.353 | 10.495 | 1.9606 | 0.0394 | Spray-CVD |
| 5.35 | 10.48 | 1.959 | 0.0410 | Evaporated film [14] |
| 5.351 | 10.484 | 1.9593 | 0.0407 | JCPDS card 25-0297: Single-crystal from the elements |

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| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE December 2002 | | 3. REPORT TYPE AND DATES COVERED Technical Memorandum |
| 4. TITLE AND SUBTITLE Ternary Precursors for Depositing I-III-VI ₂ Thin Films for Solar Cells Via Spray CVD | | | 5. FUNDING NUMBERS WU-755-A4-01-00 | |
| 6. AUTHOR(S) K.K. Banger, J.A. Hollingsworth, M. H.-C. Jin, J.D. Harris, S.A. Duraj, M. Smith, D. Scheiman, E.W. Bohannon, J.A. Switzer, W.E. Buhro, and A.F. Hepp | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191 | | | 8. PERFORMING ORGANIZATION REPORT NUMBER E-13665 | |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001 | | | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-2002-211994 | |
| 11. SUPPLEMENTARY NOTES K.K. Banger, M. H.-C. Jin, M. Smith, and D. Scheiman, Ohio Aerospace Institute, Brook Park, Ohio 44142; J.A. Hollingsworth and W.E. Buhro, Washington University, St. Louis, Missouri 63130; J.D. Harris and S.A. Duraj, Cleveland State University, Cleveland, Ohio 44115; E.W. Bohannon and J.A. Switzer, University of Missouri at Rolla, Rolla, Missouri 65404; A.F. Hepp, NASA Glenn Research Center, Cleveland, Ohio. Responsible person, A.F. Hepp, organization code 5410, 216-433-3835. | | | | |
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| 13. ABSTRACT (Maximum 200 words) The development of thin-film solar cells on flexible, lightweight, space-qualified substrates provides an attractive cost solution to fabricating solar arrays with high specific power (W/kg). Thin-film fabrication studies demonstrate that ternary single source precursors (SSP's) can be used in either a hot or cold-wall spray chemical vapour deposition (CVD) reactor, for depositing CuInS ₂ , CuGaS ₂ , and CuGaInS ₂ at reduced temperatures (400 to 450 °C), which display good electrical and optical properties suitable for photovoltaic (PV) devices. X-ray diffraction studies, energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) confirmed the formation of the single phase CIS, CGS, CIGS thin-films on various substrates at reduced temperatures. | | | | |
| 14. SUBJECT TERMS Chemical vapor deposition; Chalcopyrite; Thin film technology; Solar cells | | | 15. NUMBER OF PAGES 14 | |
| | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT Unclassified | 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified | 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified | 20. LIMITATION OF ABSTRACT | |